





**PROCESS FOR THE PRODUCTION OF POLYISOCYANATES****Publication number:** GB1515523 (A)**Publication date:** 1978-06-28**Inventor(s):****Applicant(s):** BAYER AG**Classification:****- international:** C08G18/00; C08G18/10; C08G18/78; C08G18/79; C08G18/83; C09D175/00; C08G18/00; C09D175/00; (IPC1-7): C08G18/83; C07C127/22**- European:** C08G18/10; C08G18/78B4; C08G18/79G; C08G18/83B**Application number:** GB19750030788 19750723**Priority number(s):** DE19742436741 19740730**Also published as:** NL7508984 (A) JP51037996 (A) IT1041044 (B) FR2280662 (A1) DE2436741 (A1)

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**Abstract of GB 1515523 (A)**

1515523 Modified isocyanates BAYER AG 23 July 1975 [30 July 1974] 30788/75 Heading C2C [Also in Division C3] Modified isocyanates, which suitably have an NCO group content of 0A5 to 25% by weight, an acyl urea group content of 0A5 to 50% by weight and a carbodiimide group content of 0 to 25% by weight, may be prepared by reacting a compound containing isocyanate and carbodiimide groups with a carboxylic acid in amounts such that there are 0A2 to 1A2 gram equivalents of carboxyl groups present per gram equivalent of carbodiimide groups initially present. The compound containing isocyanate and carbodiimide groups may be one obtained by subjecting a polyisocyanate, which may be a polyurethane prepolymer, to partial carbodiimide formation. Particularly preferred carboxylic acids are aliphatic carboxylic acids containing 1 to 18 carbon atoms.; Polyurethanes may be prepared from the modified polyisocyanates by conventional means.

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# PATENT SPECIFICATION

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## (54) A PROCESS FOR THE PRODUCTION OF MODIFIED POLYISOCYANATES

(71) We, BAYER AKTIENGESELL-  
 SCHAFT, a body corporate organised under  
 the laws of Germany, of 509 Leverkusen,  
 Germany, do hereby declare the invention, for  
 which we pray that a patent may be granted  
 to us, and the method by which it is to be  
 performed, to be particularly described in and  
 by the following statement:—

This invention relates to a process for the  
 production of new modified polyisocyanates  
 containing acylated urea groups, and to the  
 compounds obtained by this process.

It is known that polyisocyanates can be  
 reacted in the presence of phosphorus-contain-  
 ing catalysts to form polyisocyanates carbo-  
 diimides which, as a rule, are substantially  
 insoluble in organic solvents, as described in  
 U.S. Patent Specification 2,941,966. The reac-  
 tion is accompanied by the elimination of  
 carbon dioxide. The polyisocyanate carbo-  
 diimides thus obtained are partly branched or  
 even crosslinked by adduct formation of carbo-  
 diimide groups with isocyanate groups to form  
 uretidindione imines, or even by dimerisation  
 or carbodiimide groups to form uretidindione  
 diimines. It is also known that carboxylic acids  
 can be reacted in an addition reaction with  
 isocyanates to form amides and with carbo-  
 diimides to form acyl ureas.

Prepolymeric polyisocyanates containing  
 acylated urea groups, of the kind obtained  
 by the addition of carboxyl groups to carbo-  
 diimide groups, have never been reported.  
 Neither had it been expected that compounds  
 of this kind would be obtained by the addition  
 of carboxyl groups to polyisocyanates contain-  
 ing carbodiimide groups, because the undesir-  
 able addition reaction between carboxyl and  
 isocyanate groups i.e. undesirable for the pro-  
 duction of these compounds, had been  
 expected to accompany the desirable addition  
 reaction between carbodiimide groups and  
 carboxyl groups. The fact that the process

according to the invention can be carried out  
 at all would appear to be surprising because  
 carboxylic acid anhydrides are known to be  
 formed by the reaction of compounds con-  
 taining carbodiimide groups with carboxylic  
 acids (cf. for example F. Kurzer and K.  
 Douraghi-Zadeh, Chem. Reviews 67, 107  
 (1967).

However, it has now surprisingly been found  
 that polyisocyanato carbodimides and poly-  
 isocyanato polycarbodiimides differing widely  
 in their composition can be reacted with  
 carboxylic acids, with the isocyanate groups  
 and carbodiimide groups substantially intact,  
 to form polyacyl ureas which are soluble in a  
 variety of different solvents and which there-  
 after may contain different proportions of  
 carbodiimide groups. Finally, it was particu-  
 larly surprising to find that it is possible, in  
 accordance with this principle of the selective  
 addition of carboxylic acids to polyisocyanates  
 containing carbodiimide groups, to obtain new  
 modified polyisocyanates having properties  
 which are extremely beneficial to their sub-  
 sequent use as components in the synthesis of  
 polyurethane plastics and which, in addition,  
 can optimally be easily adapted to the applica-  
 tion envisaged through the simple variability  
 of the addition process according to the inven-  
 tion. For example, fatty acid radicals increase  
 to a considerable extent the solubility of the  
 end products of the process in apolar solvents.  
 Another advantage is the fact that additional  
 functional groups can be readily introduced  
 during the carboxylic acid addition to the  
 carbodiimide groups. For example, cross-  
 linkable groups can be built in by using  
 unsaturated carboxylic acids. The end pro-  
 ducts of the process according to the inven-  
 tion can be used with advantage for modify-  
 ing polyurethanes, although they themselves  
 represent relatively high molecular weight  
 compounds which are eminently suitable for

producing for example air-drying coatings, lacquer finishes and impregnations.

The present invention relates to a process for the production of modified isocyanates, distinguished by the fact that compounds containing isocyanate and carbodiimide groups are reacted with carboxylic acids in such quantities that from 0.2 to 1.2 gram equivalents of carboxyl groups are present in the reaction mixture per gram equivalent of carbodiimide groups.

The invention also relates to the modified polyisocyanate obtained by this process.

Starting materials suitable for use in the process according to the invention are carbodiimides containing isocyanate groups.

Isocyanates containing carbodiimide groups suitable for use in the process according to the invention can be obtained in known manner by subjecting organic polyisocyanates to partial carbodiimide formation. This partial carbodiimide formation is preferably carried out by mixing the polyisocyanate with a suitable carbodiimide forming catalyst, accompanied or followed by heating of the mixture. In general, the carbodiimide-forming reaction takes place at temperatures in the range of from 0 to 220°C. The carbodiimide-forming reaction can be carried out in the absence of or even in the presence of suitable inert solvents. The degree of carbodiimide formation reached during the carbodiimide-forming reaction can readily be determined from the quantity of carbon dioxide given off. The process according to the invention, i.e. reaction of the thus obtained carbodiimide polyisocyanate with the organic carboxylic acid is preferably carried out in a one-pot reaction by adding the acid to the reaction mixture when the required degree of carbodiimide formation is reached. The process according to the invention can also be carried out in the absence or even in the presence of solvents. The process according to the invention is generally carried out at reaction temperatures in the range from 0 to 150°C, preferably at temperatures in the range from 20 to 80°C.

Polyisocyanates suitable for use in the process according to the invention are organic compounds containing at least two isocyanate groups. Preferred polyisocyanates are polyisocyanates corresponding to the general formula:



in which:

Q represents an aliphatic hydrocarbon radical with 2 to 18 carbon atoms; a cycloaliphatic hydrocarbon radical with 4 to 14 carbon atoms, an aromatic hydrocarbon radical with 6 to 14 carbon atoms or an araliphatic hydrocarbon radical with 7 to 14 carbon atoms, and  
b is 2 or 3.

The corresponding diisocyanates are particularly preferred. It is also possible to use modified polyisocyanates, for example, polyisocyanates containing biuret, allophanate, isocyanurate, urethane or carbodiimide groups. Another preferred group of polyisocyanates used in the process according to the invention are reaction products containing isocyanate groups (NCO-prepolymers) of the kind obtained in known manner by reacting the aforementioned polyisocyanates corresponding to the formula



with deficit of polyhydroxyl compounds, especially dihydroxy or trihydroxy alkanes, having a molecular weight below 200, or with the polyhydroxy polyesters and polyethers known *per se* in polyurethane chemistry. Mixtures of the aforementioned polyisocyanates can of course also be used in the process according to the invention.

Polyisocyanates suitable for use in the process according to the invention are, for example, 1,4 - tetramethylene diisocyanate, 1,6 - hexamethylene diisocyanate, 1,12 - dodecane diisocyanate, cyclohexane - 1,3- and 1,4 - diisocyanate, and any mixture of these isomers, 1 - isocyanato - 3,3,5 - trimethyl - 5 - isocyanatomethyl cyclohexane, 1,3- and 1,4 - phenylene diisocyanate, 2,4- and 2,6 - tolylene diisocyanate and any mixture of these isomers, *m* - xylylene diisocyanate, 2,4- and 2,6 - hexahydro tolylene diisocyanate and any mixture of these isomers, 4,4' - diisocyanato dicyclohexyl methane; diphenyl methane - 4,4' - diisocyanate, naphthylene - 1,5 - diisocyanate, polyisocyanate containing carbodiimide isocyanate adducts, of the kind obtained in accordance with German Patent Specification 1,092,007, diisocyanates of the kind described in U.S. Patent Specification 3,492,330, polyisocyanates containing allophanate groups of the type described in British Patent Specification 994,890, Belgian Patent Specification 761,626 and published Dutch Patent Application 7,102,524, polyisocyanates containing isocyanurate groups of the type described in German Patent Specifications 1,022,789 and 1,027,394 and in German Offenlegungsschriften 1,929,034 and 2,004,048, polyisocyanates containing biuret groups of the type described in German Patent Specification 1,101,394, in British Patent Specification 889,050 and in French Patent Specification 7,017,514, polyisocyanates obtained by telomerisation reactions of the type described in Belgian Patent Specification 723,640, polyisocyanates containing ester groups according to British Patent Specifications 956,474 and 1,072,956 also aliphatic cycloaliphatic, araliphatic or aromatic polyisocyanates of the kind mentioned by W. Sieffen in Justus Liebig's Annalen der Chemie, 562, pages 75

to 136, reaction products of the aforementioned isocyanates with acetals according to German Patent Specification 1,072,385, isocyanates of the kind mentioned in German Patent Specification 1,022,789 and 1,027,394.

As a rule it is particularly preferred to use the commercially readily available polyisocyanates, for example 2,4- and 2,6- tolylene diisocyanate and any mixture of these isomers, and polyphenyl - polymethylene - polyisocyanates of the type obtained by condensing aniline with formaldehyde, followed by phosgenation.

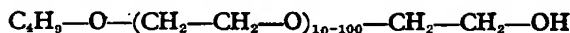
Other preferred isocyanates include 1,4 - tetramethylene diisocyanate, 1,6 - hexamethylene diisocyanate, 1 - isocyanato - 3,3,5 - trimethyl - 5 - isocyanatomethyl cyclohexane, *m* - xylylene diisocyanate and 4,4' - diisocyanato dicyclohexyl methane, 4,4' - diisocyanato diphenyl methane, 1,3 - phenylene diisocyanate, 1,4 - phenylene diisocyanate, 4,4' - diisocyanato diphenyl ether, 1,5 - naphthylene diisocyanate, 1 - methoxy phenyl - 2,4 - diisocyanate, 4,4' - biphenylene diisocyanate, 3,3' - dimethoxy - 4,4' - biphenyl diisocyanate, 3,3' - dimethyl - 4,4' - biphenyl diisocyanate, 3,3' - dimethyl diphenyl methane - 4,4' - diisocyanate.

Polyhydroxyl compounds suitable for use in the production of NCO prepolymers which are also preferably used in the process according to the invention are in particular alkane diols and triols having molecular weights below 200, for example ethylene glycol, propylene glycol, hexamethylene diol, glycerol, trimethylol propane, trimethylol ethane or mixtures of these compounds, also polyhydroxyl polyesters or polyethers having molecular

weights in the range of from 400 to 4000, of the type obtainable in known manner by reacting polybasic acids for example, adipic acid, phthalic acid, tetrahydrophthalic acid or hexahydrophthalic acid with excess quantities of the alkane diols or triols mentioned by way of example above, or by alkoxylating suitable starter molecules for example, water, ammonia, aniline or the alkane diols and triols mentioned by way of example above with alkylene oxides for example, ethylene oxide and/or propylene oxide.

In addition to these preferred NCO prepolymers, it is also possible to use in the process according to the invention NCO prepolymers of the kind obtained by reacting the isocyanates mentioned by way of example above with deficits of polyester amides, polythioethers, polyurethanes, polyacetals or polycarbonates containing hydroxyl, sulphydryl or amino groups.

Generally, any organic compounds having free carboxyl groups but no other groups likely to interfere with the reaction according to the invention, are suitable for the process according to the invention. Examples of these acids include formic acid, acetic acid, chloroacetic acid, phenyl acetic acid, propionic acid, lauric acid, palmitic acid, stearic acid, cyclohexane carboxylic acid, acrylic acid, methacrylic acid, crotonic acid, sorbic acid, 10 - undecenic acid, oleic acid, linoleic acid, cinnamic acid, abietic acid, 4 - dimethyl amino benzoic acid or even monoesters or monoamides of various dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, maleic acid, fumaric acid, phthalic acid, reaction products of



with cyclic anhydrides to form high molecular weight monocarboxylic acid semiesters, also polycarboxylic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, 2,2,4- and 2,4,4 - trimethyl adipic acid, heptadecane - 1,8- and 1,9 - dicarboxylic acid, fumaric acid, benzene - 1,3- and 1,4 - dicarboxylic acid and 1,2,2 - trimethyl cyclopentane - 1,3 - dicarboxylic acid.

Particularly suitable carboxylic acids are those corresponding to the general formula:



in which:

R represents an optionally olefinically unsaturated aliphatic hydrocarbon radical with 1 to 18 carbon atoms, an optionally olefinically unsaturated cycloaliphatic hydrocarbon radical with 6 to 19 carbon atoms, an aromatic hydrocarbon radical with 6 to 14 carbon atoms or an araliphatic hydrocarbon radical with 7 to 14 carbon atoms, and

*a* is a integer from 1 to 3 preferably 1 or 2.

Particularly preferred carboxylic acids are those corresponding to the above general formula in which R represents an aliphatic hydrocarbon radical with 1 to 18 carbon atoms, and *a*=1.

Suitable carbodiimide-forming catalysts are described for example in U.S. Patent Specifications 2,941,966, 2,853,518, and 2,853,473. The catalyst which is preferably used in a mixture of 1 - methyl - 1 - phospho - 2 - cyclopenten - 1 - oxide and 1 - methyl - 1 - phospho - 3 - cyclopenten - 1 - oxide. In addition to phosphorus compounds such as these, it is also possible to use other carbodiimide-forming catalysts known *per se*.

In one preferred embodiment of the process according to the invention for the production of the polyisocyanate polycarbodiimide polyaddition product, preferably aromatic diisocyanates are subjected to carbodiimide formation with, 1/100 to 2/10 of the molar quantity of the aromatic diisocyanate of phospholine oxide at temperatures in the range from 0°C

to 200°C. In order to obtain end products which are stable in storage at room temperature, the carbodiimide-forming reaction is preferably carried out at temperatures in the range from 100 to 200°C in the presence of catalysts, for example triphenyl phosphine oxide, which only develop their catalytic activity at temperatures in this elevated range. After the evolution of carbon dioxide has reached 50 to 95% of the theoretical (100% means complete conversion of the NCO groups into carbodiimide groups), the carboxylic acid is added dropwise. The quantity in which this acid is added is selected in such a way that there are from 0.2 to 1.2 and preferably from 0.5 to 1.0 mols of carboxyl groups per mol of carbon dioxide liberated.

Aliphatic and cycloaliphatic diisocyanates also react to form polycarbodiimides, although in their case temperatures above 100°C are generally necessary in order to obtain a conversion comparable to that obtained in the case of aromatic isocyanates.

As already mentioned, both the carbodiimide-forming reaction and also the addition reaction according to the invention can be carried out in the presence of or even in the absence of solvents. Examples of suitable solvents include benzene, toluene, xylene, cyclohexane, tetralin, chlorobenzene, *o*-dichlorobenzene, dimethyl formamide, methylene chloride, chloroform, perchloroethylene, ethyl acetate, butyl acetate, diethylene glycol dimethyl ether, tetrahydrofuran, isopropanol, tert.-butanol, acetone, methyl ethyl ketone, methyl isopropyl ketone, cyclohexane, and solvent mixtures. The polyisocyanate polyaddition product prepared in the absence of solvents often hardens to form a hard foam which, when ground into a powder, dissolves even after several days' storage at room temperature in such solvents as toluene, xylene, methylene chloride, *o*-dichlorobenzene or dimethyl formamide.

The process according to the invention opens up a fundamentally new possibility of obtaining modified polyisocyanates whose physical and service properties, such as hydrophobicity and hydrophilicity, solubility, reactivity with compounds containing isocyanate-reactive hydrogen atoms, just like the properties of the polyurethanes ultimately obtained from the new polyisocyanates (for example hardness or thermoplasticity) can readily be varied within a wide range by suitably selecting the starting isocyanates, degree of carbodiimide formation or the type and quantity of carboxylic acid added. Thus, the solubility of polycarbodiimides containing isocyanate groups in organic solvents can readily be increased by adding a long-chain fatty acid. Thermoplastic polyurethanes are obtained in particular when relatively long-chain difunctional NCO prepolymers are used

in the carbodiimide forming reaction. In cases where insufficient carboxylic acid, based on the carbodiimide groups present, is used, modified polyisocyanates still containing free carbodiimide groups are obtained. Since carbodiimides are known to stabilise plastics containing ester groups against the effect of heat and moisture, isocyanates of this kind are eminently suitable for the production of polyester urethanes having built-in ester stabilisers. Reaction of the isocyanates containing carbodiimide groups with polycarboxylic acids, especially dicarboxylic acids, in quantities corresponding to a molar ratio of carboxyl groups to carbodiimide groups of greater than 1.2 results in the formation of relatively high molecular weight and high molecular weight reaction products through the intermediate stage of the polyisocyanates according to the invention formed as intermediates. If the polycarboxylic acids are used in such quantities that there is one carboxyl group available for each carbodiimide group and for each isocyanate group, high molecular weight polyaddition products free from isocyanate groups are formed.

The preferred end products of the process according to the invention are characterised by

- a) an isocyanate group content of from 0.5 to 25% by weight, preferably from 3 to 21% by weight,
- b) an acyl urea group (which is not part of a biuret grouping) content of from 0.5 to 50% by weight preferably from 3 to 21% by weight, and
- c) an  $\text{—N=C=N—}$  group content of from 0 to 25% by weight, preferably from 0.3 to 12% by weight,

the total content of the three groups not exceeding 60% by weight.

The isocyanate content of the end products of the process according to the invention can be quantitatively determined by the titration method known *per se* using a secondary amine, for example dibutyl amine. The end product of the process dissolved in an inert solvent, for example *o*-dichlorobenzene, is reacted at room temperature with an excess of dibutyl amine. The amine consumption which can subsequently be determined by titration corresponds to the quantity of isocyanate groups present in the end products, because guanidine groups are formed from the carbodiimide groups and the secondary amine and can also be titrated, for example, with hydrochloric acid, so that they do not enter the overall balance of the titrimetric NCO-determination.

In order to determine the carbodiimide groups, reaction of the end products with secondary amine (diethyl amine) is followed by removal of the amine excess and solvent

by distillation. The guanidine groups formed are then quantitatively determined directly by titration, for example with hydrochloric acid. This titration is not affected by the urea groups formed (isocyanate groups plus secondary amine).

The acylated urea group content of the end products of the process according to the invention can be calculated from the difference in the carbodiimide content before and after the reaction according to the invention with carboxylic acids. The fact that, in the process according to the invention, the expected reaction leading to acyl urea groups also takes place between the carbodiimide groups and the carboxyl groups, can be seen from the IR-bands at  $1720\text{ cm}^{-1}$  and  $1660\text{ cm}^{-1}$  which can always be observed in the end products of the process according to the invention and which are typical of the acyl urea group.

The end products of the process according to the invention are suitable for use as starting materials in the production of polyurethane plastics by the isocyanate polyaddition process. High-quality plastics are obtained by the chain-extending reaction known *per se* with suitable chain extenders. The end product of the process according to the invention are preferably used in the production of coatings and lacquer finishes by the isocyanate polyaddition process.

#### EXAMPLE 1

34 parts by weight (0.02 mol) of an adipic acid - 1,6 - hexanediol, neopentyl glycol polyester having an OH number of 65 are dehydrated for 30 minutes in a water jet pump vacuum at a temperature of  $120^{\circ}\text{C}$ , and subsequently left to react for 30 minutes at that temperature with 34.8 parts by weight (0.2 mol) of a mixture of 2,4- and 2,6 - tolylene diisocyanate in a ratio of 8:2 (NCO-content of the resulting mixture 21.8% by weight). After dilution with 69.2 parts by weight of toluene, 0.5 parts by weight (4.3 mMol) of a mixture of 1 - methyl - 1 - phospho - 2- and 3 - cyclopenten - 1 - oxide are added, followed by the gradual dropwise addition at room temperature of 25 parts by weight (0.125 mol) of lauric acid in 28 parts by weight of toluene after 3.1 litres of carbon dioxide (0.138 mol) have been given off. A 48% solution of a polyisocyanate polycarbodiimide polyacyl urea having free NCO groups is obtained. This solution is applied to a substrate, and following evaporation of the solvent by reaction with atmospheric moisture a clear elastic film remains.

Analysis of the dissolved product (all percentages relate to solid substance):

—NCO:	3.5% by weight
—N=C=N—:	0.9% by weight
—CO—N—CO—NH—:	11.5% by weight

#### EXAMPLE 2

The reaction is carried out in the same way as in Example 1, except that 8.9 parts by weight (5 mMol) of the adipic acid - 1,6 - hexanediol, neopentyl glycol polyester are replaced by 0.52 parts by weight (5 mMol) of 2,2 - dimethyl - 1,3 - propanediol. The resulting solution is applied to a substrate, and following evaporation of the solvent by reaction with atmospheric moisture at room temperature a clear hard film remains.

Analysis of the dissolved product (all percentages relate to solid substance):

—NCO:	3.1% by weight
—N=C=N—:	1.6% by weight
—CO—N—CO—NH—:	11.1% by weight

#### EXAMPLE 3

34.8 parts by weight (0.2 mol) of a mixture of 2,4- and 2,6 - tolylene diisocyanate in a ratio of 8:2 are dissolved in 81.2 parts by weight of toluene, and the resulting solution subjected to carbodiimide formation with 0.5 parts by weight of a mixture of 1 - methyl - 1 - phospho - 2- and 3 - cyclopenten - 1 - oxide. After 2.2 litres of carbon dioxide have been given off, 7.3 parts by weight (0.05 mol) of adipic acid in 7 parts by weight of dimethyl formamide are added dropwise. The resulting solution is applied to a substrate and following evaporation of the solvent by reaction with atmospheric moisture at room temperature a scratch proof slightly brittle film remains.

Analysis of the dissolved product (all percentages relate to solid substance):

—NCO:	21.0% by weight
—N=C=N—:	<1.0% by weight
—CO—N—CO—NH—:	20.5% by weight

#### EXAMPLE 4

34.8 parts by weight (0.2 mol) of a mixture of 2,4- and 2,6 - tolylene diisocyanate in a ratio of 8:2 are subjected to carbodiimide formation with 0.4 parts by weight (3.4 mMol) of a mixture of 1 - methyl - 1 - phospho - 2- and -3 - cyclopenten - 1 - oxide. After 1 litre of carbon dioxide has been given off, 10 parts by weight (0.05 mol) of lauric acid are slowly stirred into the liquid. After 24 hours, a hard foam is obtained which can readily be ground into a powder.

The powder is dissolved in toluene and following evaporation of the solvent at room temperature by cross-linking with atmospheric moisture a clear hard, slightly brittle film remains.

Analysis of the dissolved product (all percentages relate to solid substance):

—NCO:	5.0% by weight
—N=C=N—:	12.0% by weight
—CO—N—CO—NH—:	11.5% by weight

## EXAMPLE 5

63.8 parts by weight of a biuret polyisocyanate, essentially consisting of tris - (isocyanatohexyl) - biuret, having an NCO-content of 16% by weight, 34.8 parts by weight (0.2 mol) of a mixture of 2,4 - tolylene diisocyanate in a ratio of 8:2 are dissolved in 100 parts by weight of xylene and the resulting solution subjected to carbodiimide formation at 20°C with 0.4 parts by weight (3.5 mMol) of 1 - methyl - 1 - phospho - 2- and -3 - cyclopenten - 1 - oxide. After 3 litres of carbon dioxide have been given off, 27 parts by weight (0.13 mol) of lauric acid in 40 parts by weight of xylene are added dropwise. The resulting solution is applied to a substrate, and following evaporation of the solvent by reaction with atmospheric moisture at room temperature a clear hard film remains.

Analysis of the dissolved product (all percentages relate to solid substance):

—NCO: 8.0% by weight  
 —N=C=N—: 2.4% by weight  
 —CO—N—CO—NH—: 9.1% by weight

## EXAMPLE 6

44.4 parts by weight (0.2 mol) of 1 - isocyanato - 3,3,5 - trimethyl - 5 - isocyanato-methyl cyclohexane are dissolved in 103 parts by weight of *o* - dichlorobenzene and subjected to carbodiimide formation at 150°C with 0.5 parts by weight (4.3 mMol) of a mixture of 1 - methyl - 1 - phospho - 2- and 3 - cyclopenten - 1 - oxide.

After 2.2 litres of carbon dioxide have been given off, 20.2 parts by weight (0.1 mol) of sebacic acid in 47 parts by weight of *o* - dichlorobenzene are added dropwise. The resulting solution is applied to a substrate, and following evaporation of the solvent by reaction with atmospheric moisture at room temperature a scratch, extremely brittle film remains.

Analysis of the dissolved product (all percentages relate to solid substance):

—NCO: 13.8% by weight  
 —N=C=N—: 0.4% by weight  
 —CO—N—CO—NH—: 13.8% by weight

## WHAT WE CLAIM IS:—

1. A process for the production of a modified isocyanate which comprises reacting a compound containing isocyanate and carbodiimide groups with a carboxylic acid, the amount of carboxylic acid used being such that from 0.2 to 1.2 gram equivalents of carboxyl groups are present in the reaction mixture per gram equivalent of carbodiimide groups initially present.

2. A process as claimed in claim 1, in which

the carboxylic acid corresponds to the general formula



in which

R represents an aliphatic hydrocarbon radical having from 1 to 18 carbon atoms and optionally containing olefinic double bonds, a cycloaliphatic hydrocarbon radical having from 6 to 19 carbon atoms and optionally containing olefinic double bonds, an aromatic hydrocarbon radical having from 6 to 14 carbon atoms or an araliphatic hydrocarbon radical having from 7 to 14 carbon atoms, and

*a* is an integer from 1 to 3.

3. A process as claimed in claim 1 or 2, in which the compound containing isocyanate and carbodiimide groups is one obtained by subjecting an organic polyisocyanate or isocyanate mixture to partial carbodiimide formation.

4. A process as claimed in claim 3, in which the organic polyisocyanate corresponds to the general formula:



in which:

Q represents an aliphatic hydrocarbon radical having from 2 to 18 carbon atoms, a cycloaliphatic hydrocarbon radical having from 4 to 14 carbon atoms, an aromatic hydrocarbon radical having from 6 to 14 carbon atoms radicals or an araliphatic hydrocarbon radical having from 7 to 14 carbon atoms, and

*b* is 2 or 3;

or are prepolymers obtained by reacting the polyisocyanates of the formula  $Q(NCO)_b$  with deficits of polyhydroxyl compounds optionally containing ether or ester groups, or are mixtures of these prepolymers and the polyisocyanates of the formula  $Q(NCO)_b$ .

5. A process as claimed in any of claims 1 to 4, in which the reaction takes place at a temperature of from 0 to 150°C.

6. A process for the production of modified isocyanates substantially as herein described with reference to any of the specific Examples.

7. A modified isocyanate when produced by a process as claimed in any of claims 1 to 6.

8. A modified isocyanate having an isocyanate group content of from 0.5 to 25% by weight an acylurea group (which is not part of a biuret grouping) content of from 0.5 to 50% by weight and an —N=C=N— group content of from 0 to 25% by weight, the total content of the three groups not exceeding 60% by weight.

9. A modified isocyanate as claimed in claim 8 in which the isocyanate group

content is from 3 to 21% by weight, the acyl-urea group content is from 0.3 to 12% by weight.

- 5 10. A modified isocyanate substantially as herein described with reference to any of the specific Examples.

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